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RMRS Rocky Mountain Remediation Services, L.L.C.
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INTEROFFICE MEMORANDUM

DATE: September 26, 1995

TO: A. L. Primrose, Sitewide Actions, Bldg. 080, X8618

FROM: M. A. Siders, Hydrogeology, Bldg. 080, X6933 MAS

SUBJECT: RADIUM ANOMALIES IN ROCKY FLATS SOILS - MAS-016-95

DOE Order: 4700.1

Action: None

The attached report includes an evaluation of data from radium and uranium in Rocky Flats surface and subsurface soils. A brief summary on the geochemistry and radium, as well as uranium and thorium, is also presented. Figures of the correlations between radium-226 (daughter isotope) and uranium-233,234 and uranium-238 (parents) are provided for site (OU 4 and OU 1) and background data sets.

Please feel free to contact me if you have any questions.

rap

cc:
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B. L. Roberts
R. S. Roberts
ER Project File (2)

ADMIN RECORD

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BZ-A-000351

1.0 INTRODUCTION

During the recent IHSS Prioritization program, the sitewide data for surface and subsurface soils were screened against the 99/99 upper tolerance limits (99/99 UTLs) for background data, and against the preliminary programmatic remediation goals (PPRGs) calculated for office workers, construction workers, and open-space users. Some anomalies were noted for radium in surface and subsurface soils across Rocky Flats. It was also noted that the value of the 99/99 UTL is 48 times the value of the surface-soil PPRG for radium-226, under the office-worker scenario. Therefore, any data point that lies above the 99/99 UTL has a PPRG ratio (i.e., ratio of analytical result to the value of the PPRG) of at least 48; the minimum datum for background has a PPRG ratio of 4 for radium-226.

Because of the resultant high PPRG ratios for radium-226, and, to a lesser extent, radium-228, a more detailed look at radium in the environment was deemed necessary. The distribution of radium in soils across Rocky Flats was plotted and evaluated. Several significantly elevated activities of radium were noted for soil samples collected in OUs 2 and 4. In an effort to determine whether or not these higher values were of natural or anthropogenic origin, the relationships for uranium and radium in background and site areas were evaluated.

2.0 CHEMISTRY OF RADIUM

There are four, naturally occurring isotopes of radium: radium-223, radium-224, radium-266, and radium-228. Radium is an alkaline-earth metal with a geochemical behavior somewhat similar to that of barium. Radium primarily exists as the divalent cation, Ra^{+2}, in aqueous solutions. Unlike the transuranic elements, plutonium and americium, radium is less strongly bound to the solid phase and may be remobilized by infiltrating solutions. The solubility of $RaSO_4$ is reported to be somewhat less than that of barite ($BaSO_4$) (Hem, 1992). The amount of radium in solution in most natural waters is less than 1.0 pCi/L, although some deep groundwaters near Helsinki, Finland are reported to contain more than 100 pCi/L of radium-226 (Hem, 1992).

Uranium and thorium, the parents of radium-226 and radium-228, respectively, are classified as "incompatible" elements (Krauskopf, 1979). Because of their size and charge, these ions tend to be segregated into late-stage magmatic fluids during magmatic crystallization. Pegmatites, such as those found in granitic rocks along the Colorado Front Range, are the crystalline form of these late-stage magmatic fluids. These billion-year-old granitic rocks, represent a potential source of radium-226 and radium-228, through the radiogenic decay of uranium-238 and thorium-232 incorporated into pegmatite minerals .

Although uranium and thorium exhibit similar behavior in magmatic fluids, the two elements differ greatly in their behavior in aqueous solutions under near-surface conditions (Hem, 1992). Because thorium occurs only in the +4 state, whereas uranium occurs in both the +4 (less mobile) and +6 (more mobile), thorium tends to be less mobile than uranium in oxidizing alkaline systems. The oxidizing, neutral to alkaline environment at Rocky Flats should, therefore, tend to promote separation of thorium and uranium isotopes in solution.

Radium-226 is a naturally occurring disintegration product of the uranium-238 decay chain, and has a half-life of 1,620 years. Uranium-238 has a half-life of 4.51×10^9 years, decaying to thorium-234 (24.1 days), protactinium-234 (6.7 hours), uranium-234 (2.48×10^5 years), thorium-230 (7.52×10^4 years), then to radium-226, and, ultimately, to the stable isotope, lead-206 (Friedlander et al., 1964).

Unlike radium-226, which is a product of the uranium-238 decay chain, radium-228 is a disintegration product (alpha decay) of thorium-232 (half-life 1.39 x 10^{10} years). Radium-228 has a half-life of only 6.7 years. Although thorium-232 was used for several applications at Rocky Flats (ChemRisk, 1992), the 10-billion-year half-life makes it unlikely that much radium-228 would have accumulated by radiogenic decay of pure thorium-232. No thorium-232 data are available for evaluation.

3.0 RADIUM AND URANIUM AT ROCKY FLATS AND IN NEARBY AREAS

Radium-228 and radium-226 are not listed for historical usage at Rocky Flats (ChemRisk, 1992; DOE, 1992). In addition, there are abundant natural sources of uranium and radium in nearby areas, such as Coal Creek Canyon (a source area for the Rocky Flats Alluvium). However, incidental use of radium or radium-contaminated materials at Rocky Flats may not have been reported in either the Historical Release Report (DOE, 1992) or the ChemRisk report (1992).

A recent investigation by the Jefferson County Health Department measured the levels of uranium, radium, and radon (the daughter of radium decay) in groundwater wells of Coal Creek Canyon (Moody and Morse, 1992). The Jefferson County study compiled data from thirty-three domestic groundwater wells in Coal Creek Canyon. Uranium (total) ranged from 1.3 to 1,200 pCi/L, with a mean and standard deviation of 174.9 pCi/L and 339.1 pCi/L, respectively. Radium-226 ranged from 0.0 to 40.0 pCi/L, with a mean and standard deviation of 4.3 pCi/L and 9.1 pCi/L, respectively. Data for surface and subsurface soils were not collected for the Jefferson County study.

Because there exists an established source area for naturally occurring uranium and radium near Rocky Flats, correlations of radium-226 to the parent isotopes (uranium-233/234 and uranium-238) were calculated for both background and site (OU4) data sets. If a correlation between parent and daughter isotopes exists, it would represent supporting evidence for a natural source of the radium.

Linear regression analysis performed on background subsurface-soil data for radium-226 and uranium-238 yields a correlation coefficient (r) of 0.70, which indicates a moderate correlation between the dependent and independent variables (Figure 1b). The correlation coefficient for radium-226 and uranium-233+234 is lower, but still indicates some relationship (Figure 1a). The data from OU4 subsurface soils show a similar correlation ($r = 0.77$ to 0.80) between radium-226 and the uranium isotopes (Figures 2a and 2b).

Background surface-soil data (DOE, 1995) show a lesser correlation between radium-226 and the uranium isotopes (Figures 3a and 3b). Data from OU4 and the OU1 "hot spots" show correlations similar to those of background (Figures 4a, 4b and Figures 5a, 5b, respectively). If the ratios of radium-226/uranium-233,234 and radium-226/uranium-238 are plotted against radium-226 activities in data for background and OU4 subsurface soils, no striking differences are apparent (Figures 6a, 6b and Figures 7a, 7b). For background subsurface-soil data, the radium-226/uranium-233,234 ratio ranges from 0.1 to 4 (Figure 6a), whereas for OU4 subsurface-soil data, this ratio ranges from 0.2 to 0.9 (Figure 7a). Slightly narrower ranges are seen for the radium-226/uranium-238 ratios for background (0.6 to 3, Figure 6b) and OU4 (0.3 to 2, Figure 7b) data.

Data for background and OU4 surface soils also show inconclusive results for radium-226/uranium-233,234 and radium-226/uranium-238 ratios (Figures 8a, 8b and Figures 9a, 9b, respectively). Ratios for data from the OU1 hot spots were also plotted (Figures 10a and 10b); these show the greatest range. For background surface soils, the ratio of radium-226/uranium-233,234 ranges from approximately 0.2 to 1.0; for OU4 surface soils, this ratio ranges from about 0.07 to 1.0; for the OU1 hot spots, this ratio ranges from about 0.2 to 2.0. Similarly, the radium-226/uranium-238 ratio ranges from about 0.5 to 0.9 for background data, 0.09 to 1.5 for OU4 data, and 0.2 to 10 for OU1 hot-spot data.

4.0 SUMMARY AND CONCLUSIONS

As previously mentioned, there is no reference to the historic use of radium isotopes at the Rocky Flats Plant. The current data suggest that, aside from several outliers, the activities of radium-226 observed in soil samples from Rocky Flats are the result of natural processes. However, the brief review presented here cannot conclusively state whether or not the radium anomalies in Rocky Flats soils are of natural or anthropogenic origin. A more in-depth study may provide a better answer for the issue of radium-226 and radium-228 at Rocky Flats.

A literature review of data for naturally occurring radium and uranium isotopes should be the starting point of further investigations of radium at Rocky Flats. These data are necessary to provide a broader understanding of the parent-daughter relationships of these radionuclides in natural soils and waters. Next, the exact isotopic composition of uranium used at Rocky Flats should be reviewed to determine if radium impurities were contained within the uranium processed at the plant. In addition, the possible incidental use of radium or radium-contaminated materials should be evaluated. Until additional information is obtained, the origin of radium isotopes in Rocky Flats soils will remain speculative.

5.0 REFERENCES CITED

ChemRisk, 1992. Rocky Flats History: Rocky Flats Toxicologic Review and Dose Reconstruction, Task 3/4 Report.

DOE, 1992. Historical Release Report for the Rocky Flats Plant.

DOE, 1993. Background Geochemical Characterization Report.

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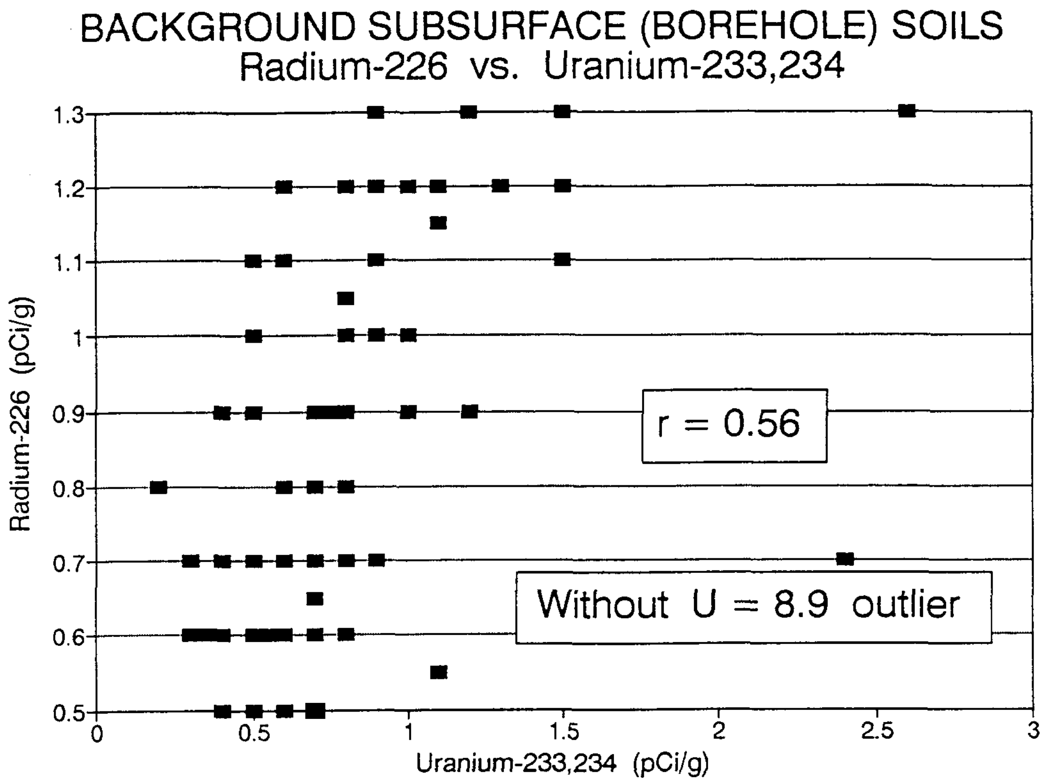
Friedlander, G., Kennedy, J.W., Miller, J.M., 1964. Nuclear and Radiochemistry. Second edition, John Wiley & Sons, Inc., N.Y., 585 pp.

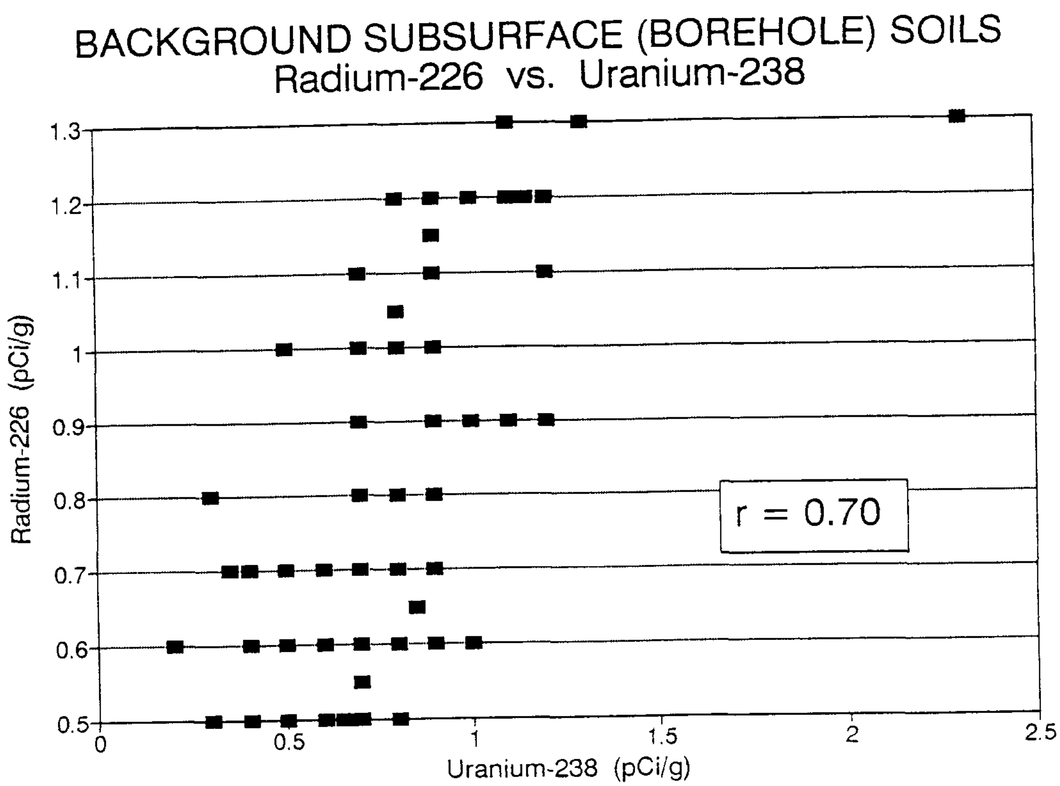
Hem, J.D., 1992. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper 2254, 263 pp.

Krauskopf, K.B., 1979. Introduction to Geochemistry. Second edition, McGraw-Hill Book Company, 617 pp.

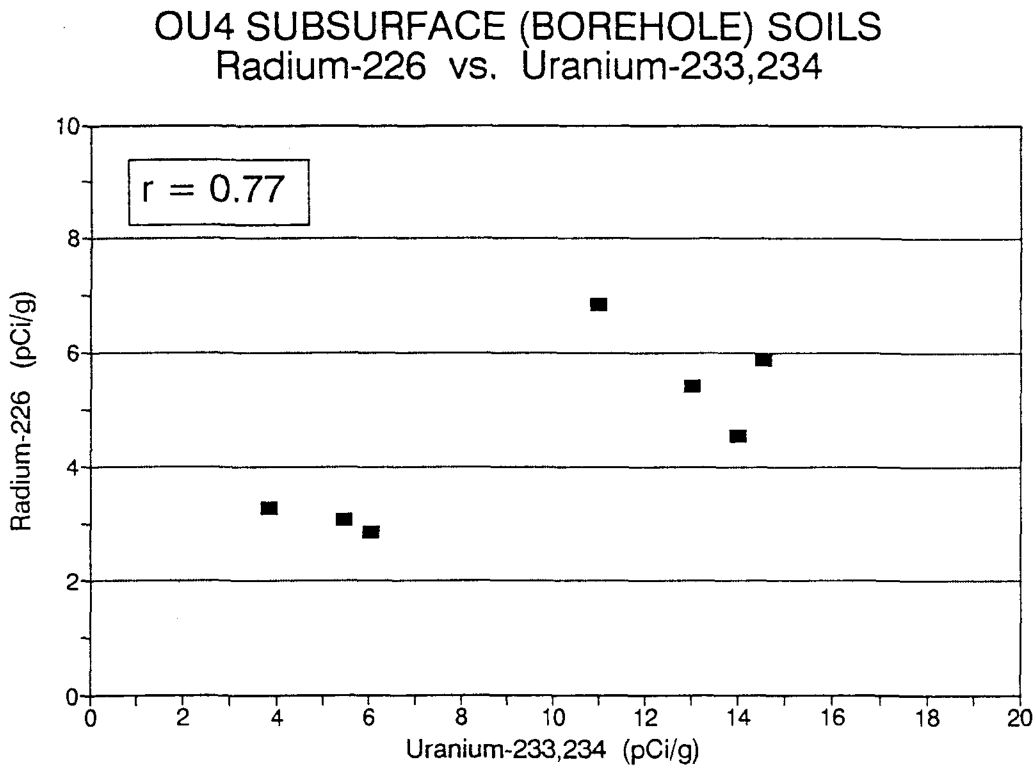
Morse, J.L. and Moody, J.S., 1992. Final Report for the State Indoor Radon Grant, Jefferson County Health Department, 21 p.


BACKGROUND SUBSURFACE (BOREHOLE) SOILS
Radium-226 vs. Uranium-233,234
Radium-226 (pCi/g)
Uranium-233,234 (pCi/g)
r = 0.56
Without U = 8.9 outlier
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0
0.5
1
1.5
2
2.5
3

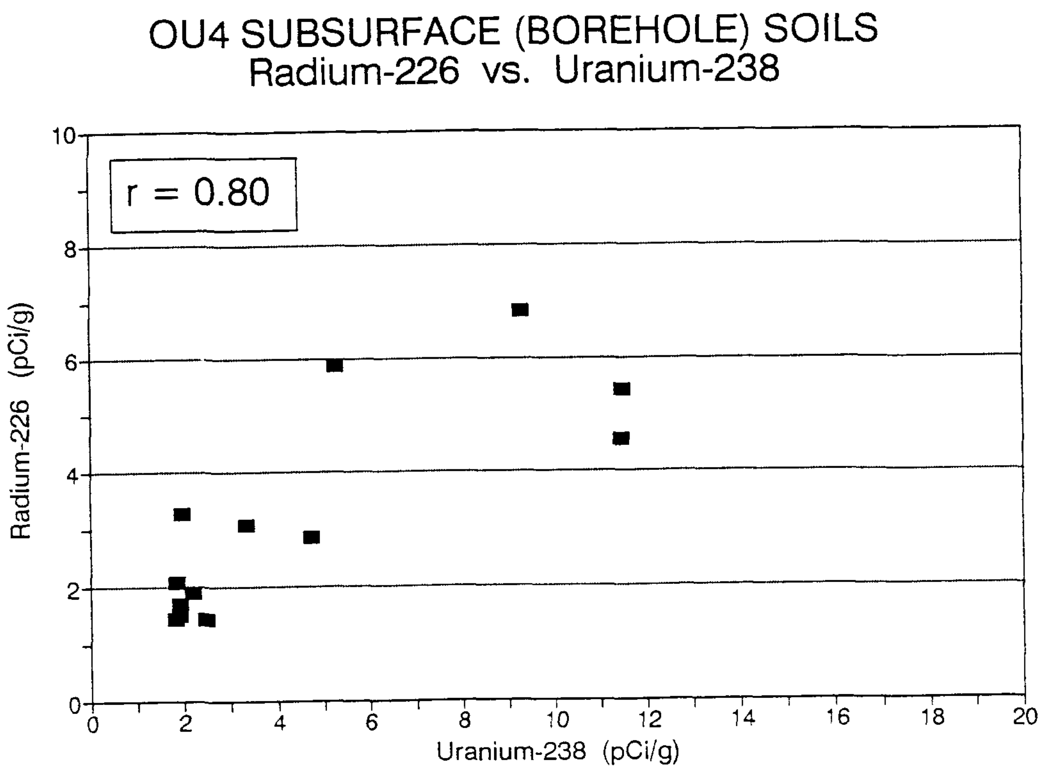
1a


BACKGROUND SUBSURFACE (BOREHOLE) SOILS
Radium-226 vs. Uranium-238
Radium-226 (pCi/g)
Uranium-238 (pCi/g)
r = 0.70
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0
0.5
1
1.5
2
2.5

1b

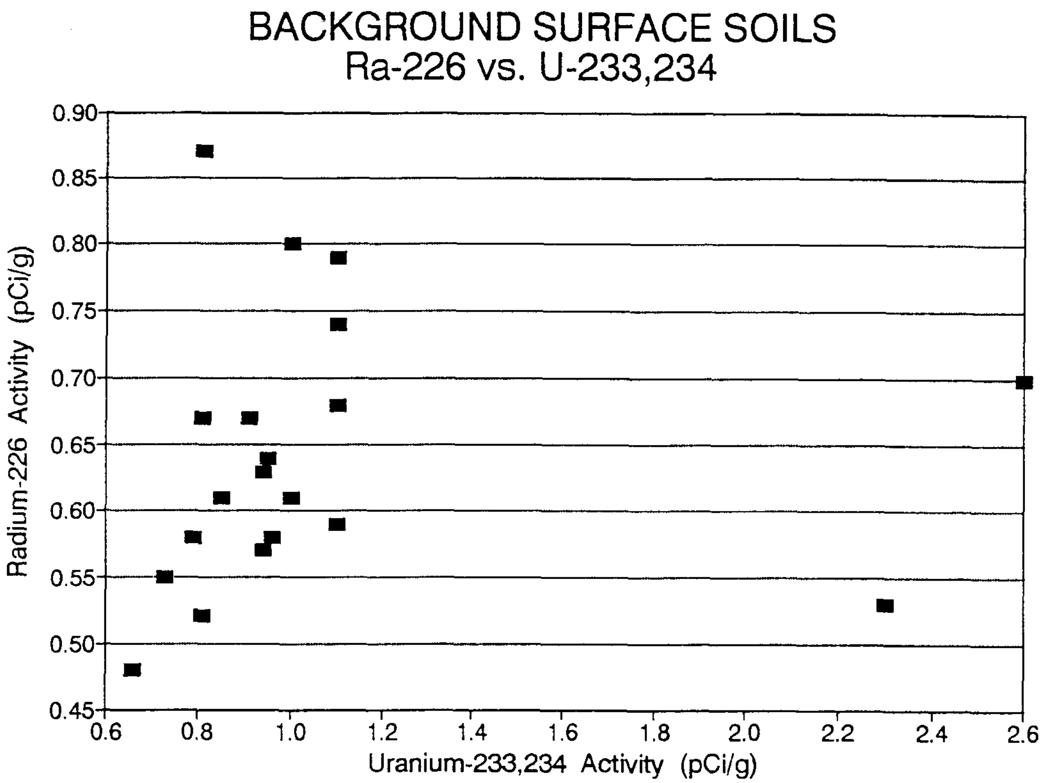

OU4 SUBSURFACE (BOREHOLE) SOILS
Radium-226 vs. Uranium-233,234
r = 0.77
Radium-226 (pCi/g)
Uranium-233,234 (pCi/g)
0
2
4
6
8
10
12
14
16
18
20

2a

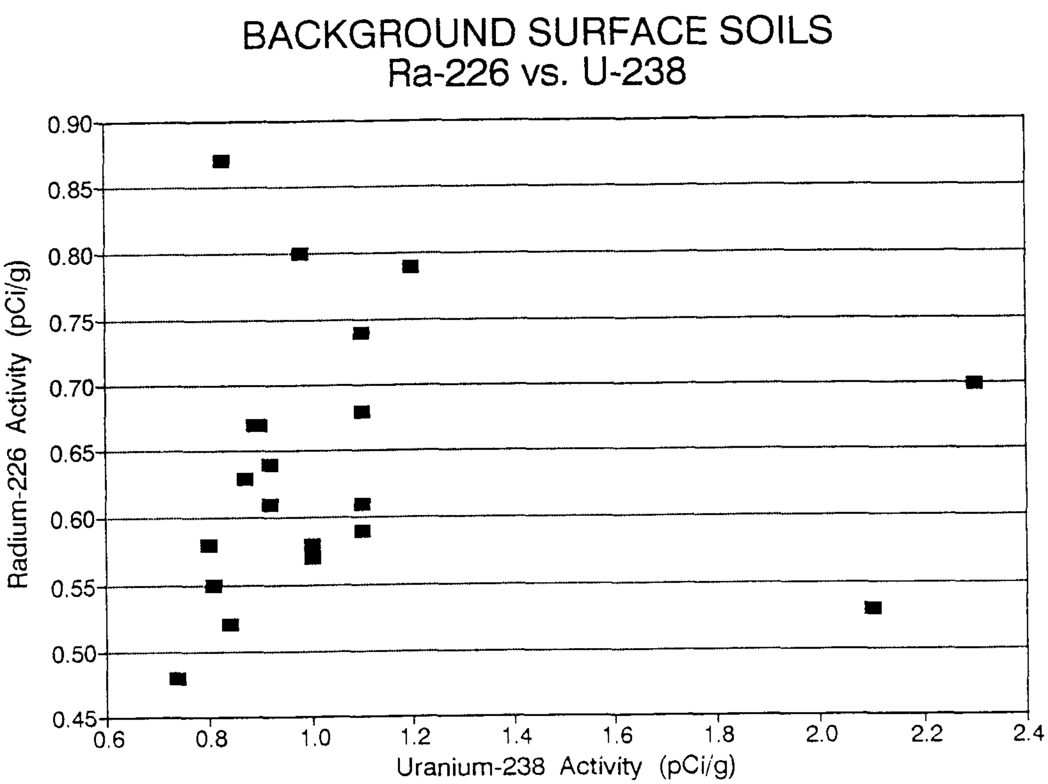

OU4 SUBSURFACE (BOREHOLE) SOILS
Radium-226 vs. Uranium-238
r = 0.80
Radium-226 (pCi/g)
Uranium-238 (pCi/g)
0
2
4
6
8
10
12
14
16
18
20

2b

7

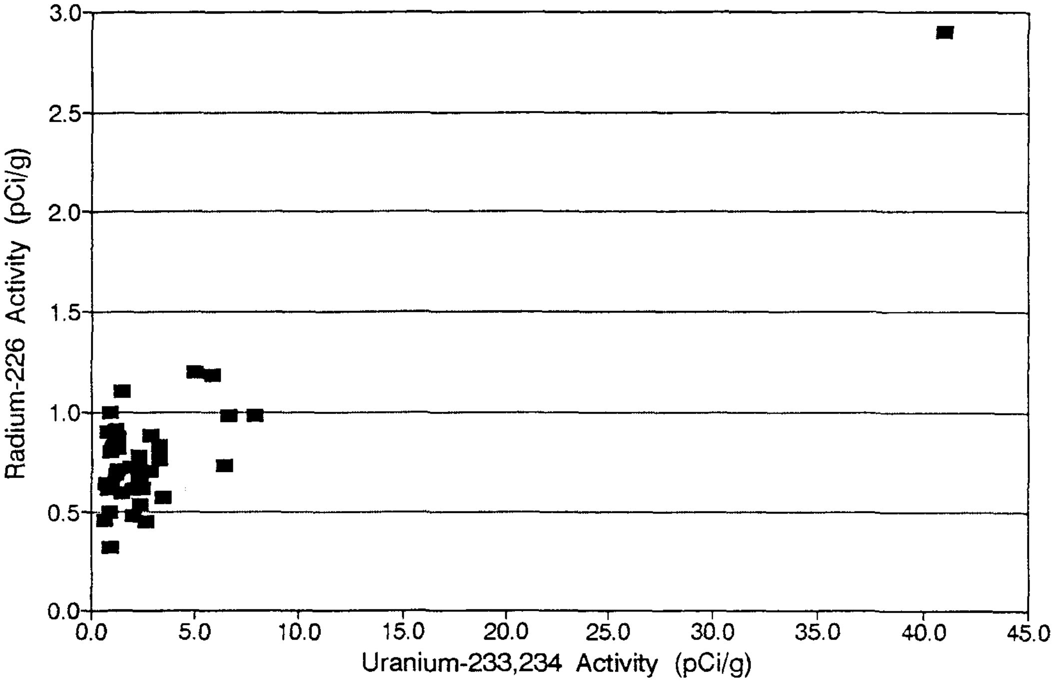

BACKGROUND SURFACE SOILS
Ra-226 vs. U-233,234
Radium-226 Activity (pCi/g)
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Uranium-233,234 Activity (pCi/g)

3a


BACKGROUND SURFACE SOILS
Ra-226 vs. U-238
Radium-226 Activity (pCi/g)
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Uranium-238 Activity (pCi/g)

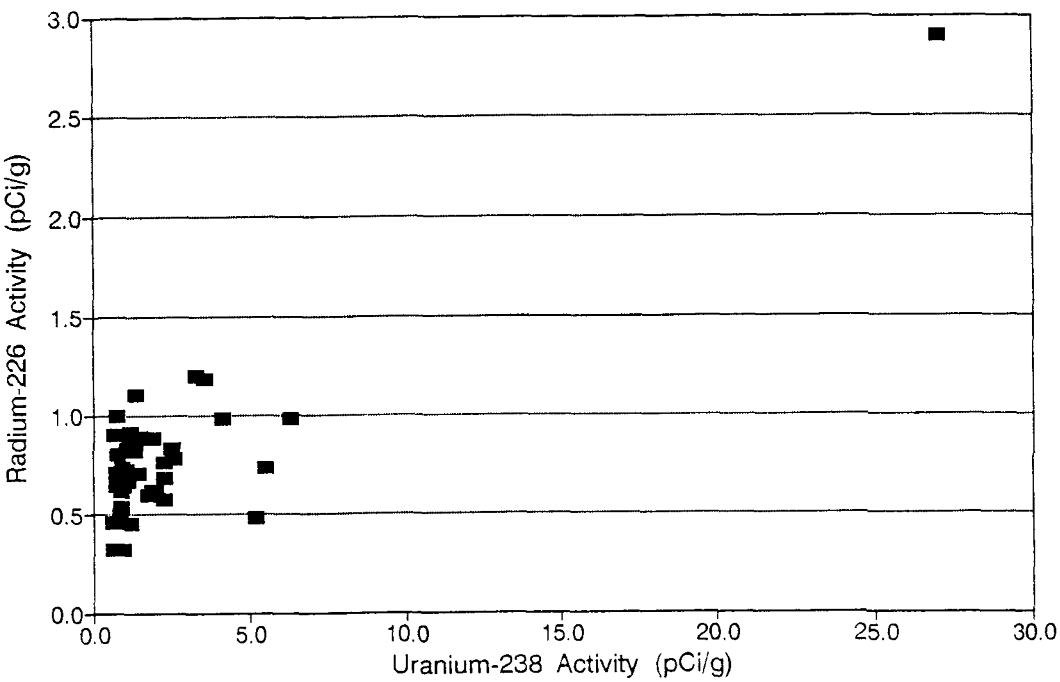
3b

OU4 SURFACE SOILS
Ra-226 vs. U-233,234

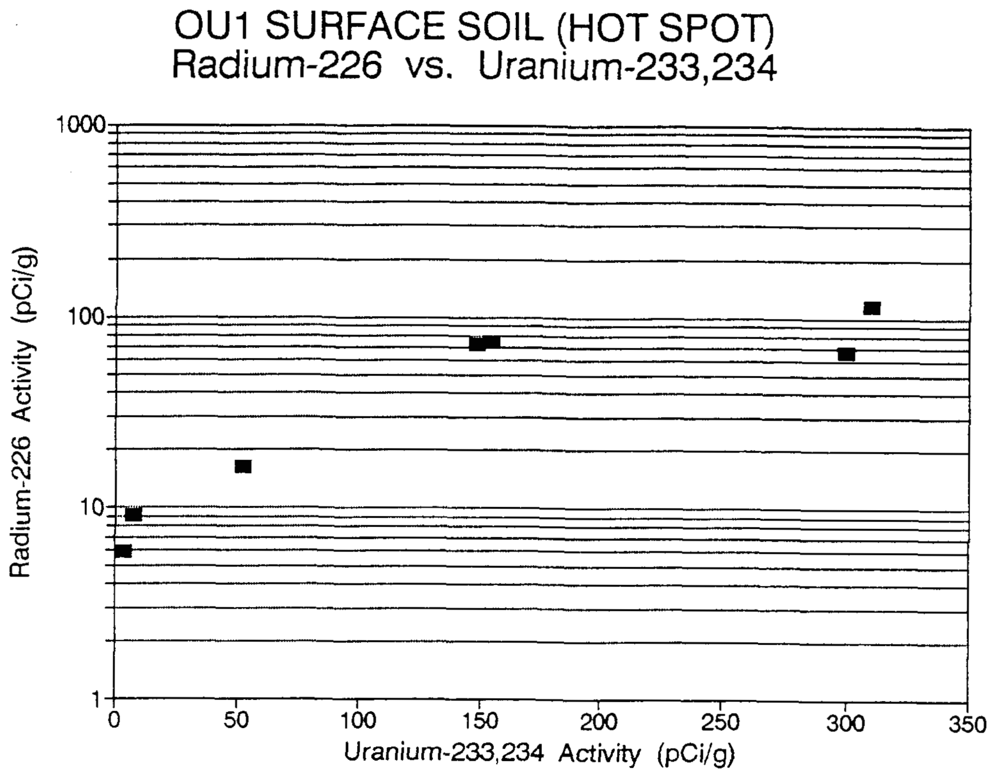


4a

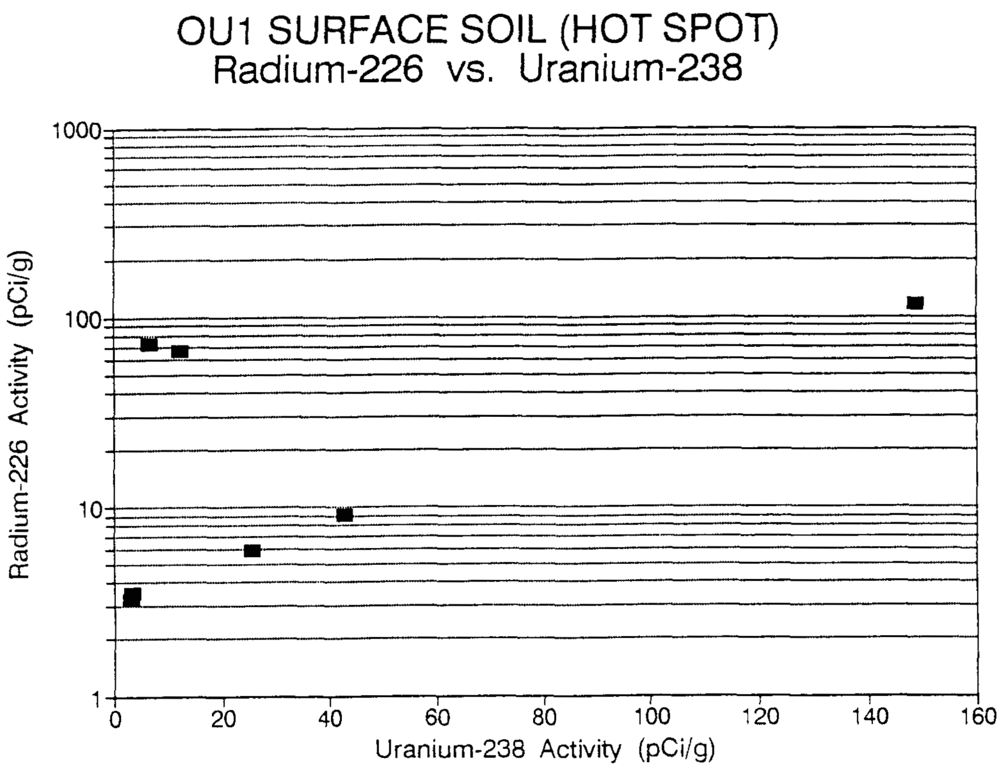
OU4 SURFACE SOILS
Ra-226 vs. U-238



4b

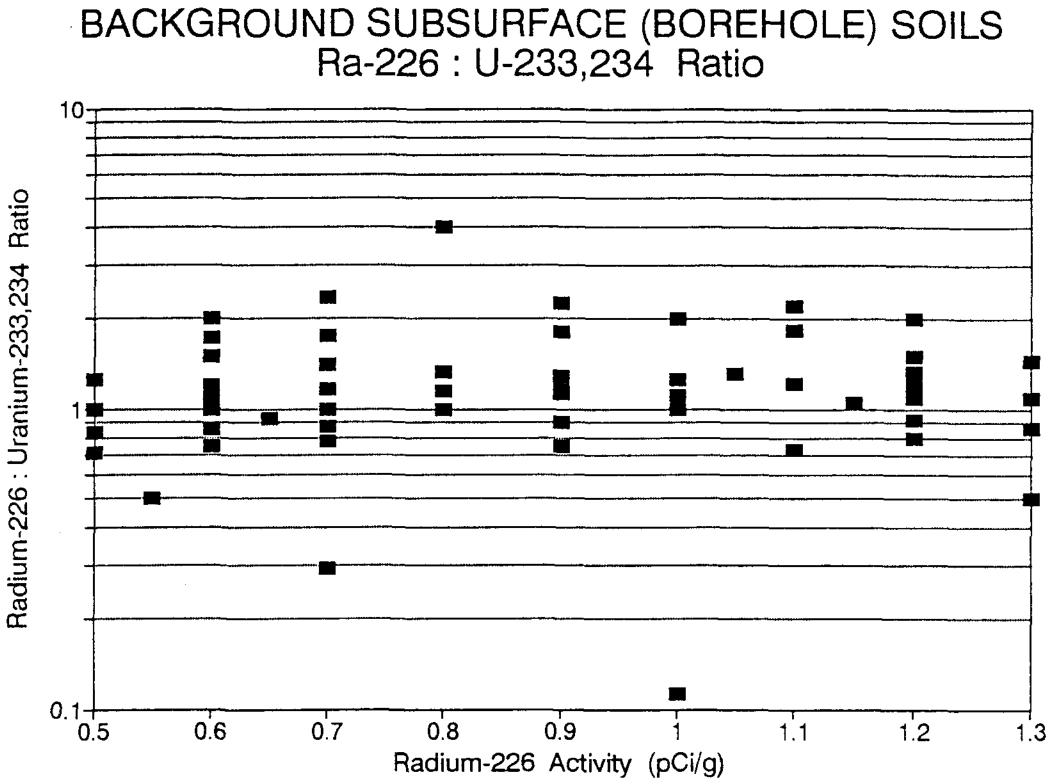

OU1 SURFACE SOIL (HOT SPOT)
Radium-226 vs. Uranium-233,234
Radium-226 Activity (pCi/g)
1000
100
10
1
0
50
100
150
200
250
300
350
Uranium-233,234 Activity (pCi/g)

5a

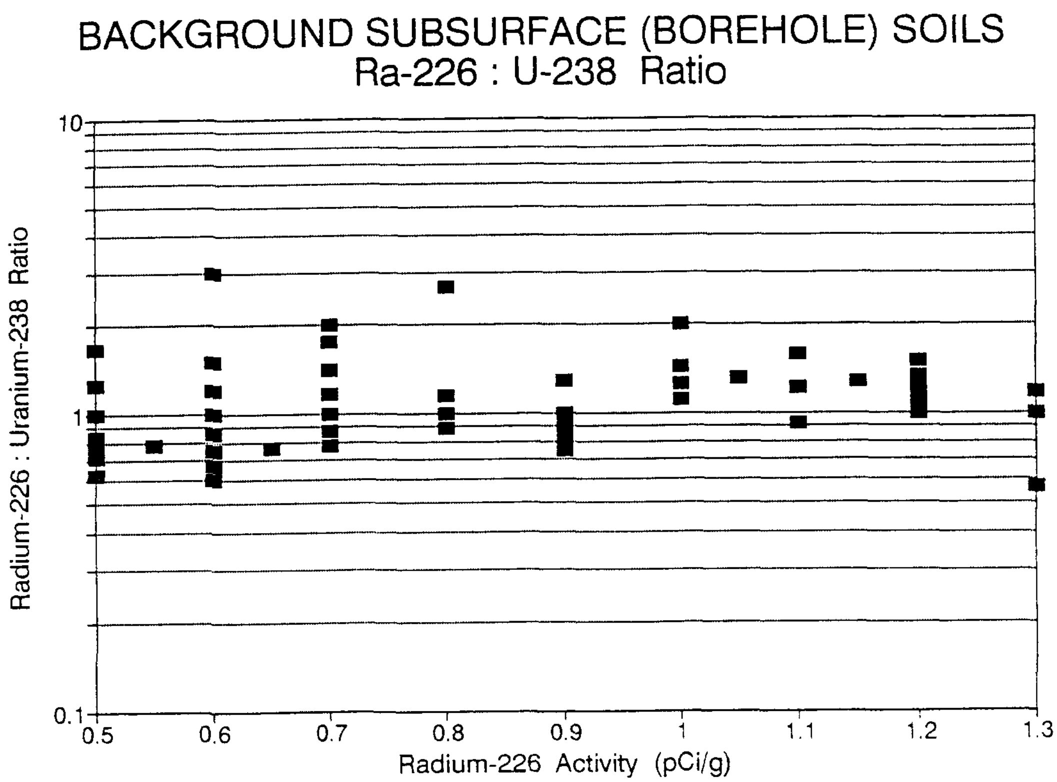

OU1 SURFACE SOIL (HOT SPOT)
Radium-226 vs. Uranium-238
Radium-226 Activity (pCi/g)
1000
100
10
1
0
20
40
60
80
100
120
140
160
Uranium-238 Activity (pCi/g)

5b

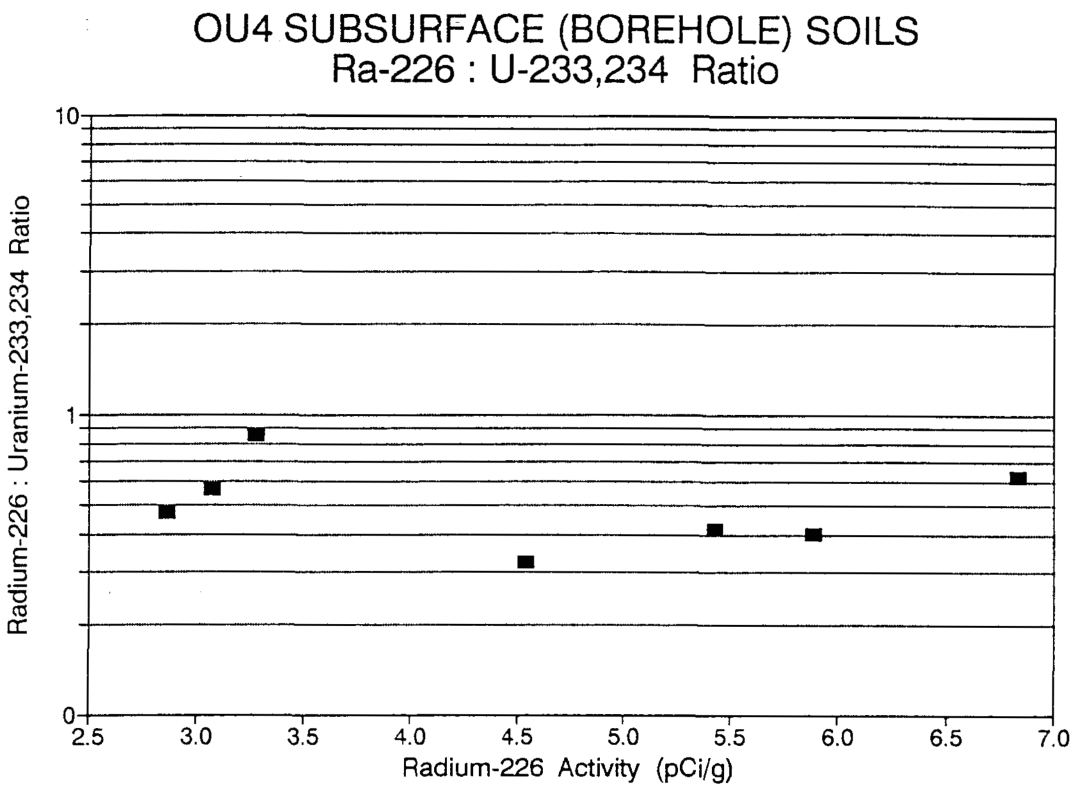
10


BACKGROUND SUBSURFACE (BOREHOLE) SOILS
Ra-226 : U-233,234 Ratio
10
1
0.1
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
Radium-226 Activity (pCi/g)
Radium-226 : Uranium-233,234 Ratio

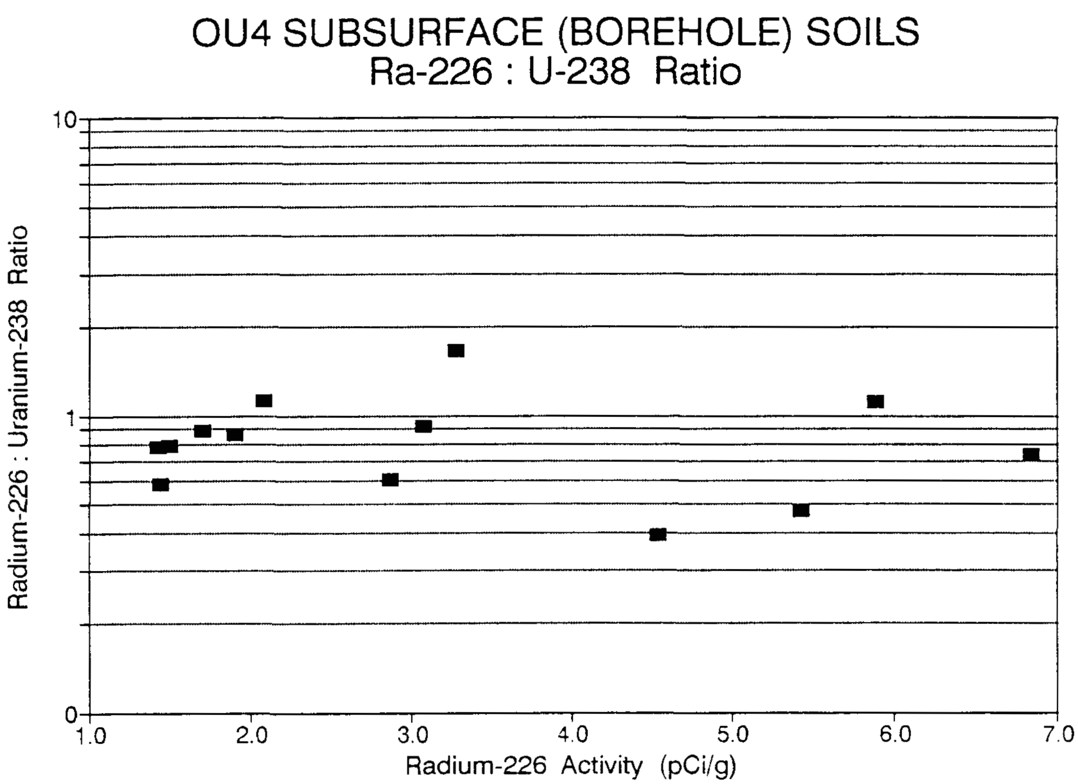
6a


BACKGROUND SUBSURFACE (BOREHOLE) SOILS
Ra-226 : U-238 Ratio
10
1
0.1
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
Radium-226 Activity (pCi/g)
Radium-226 : Uranium-238 Ratio

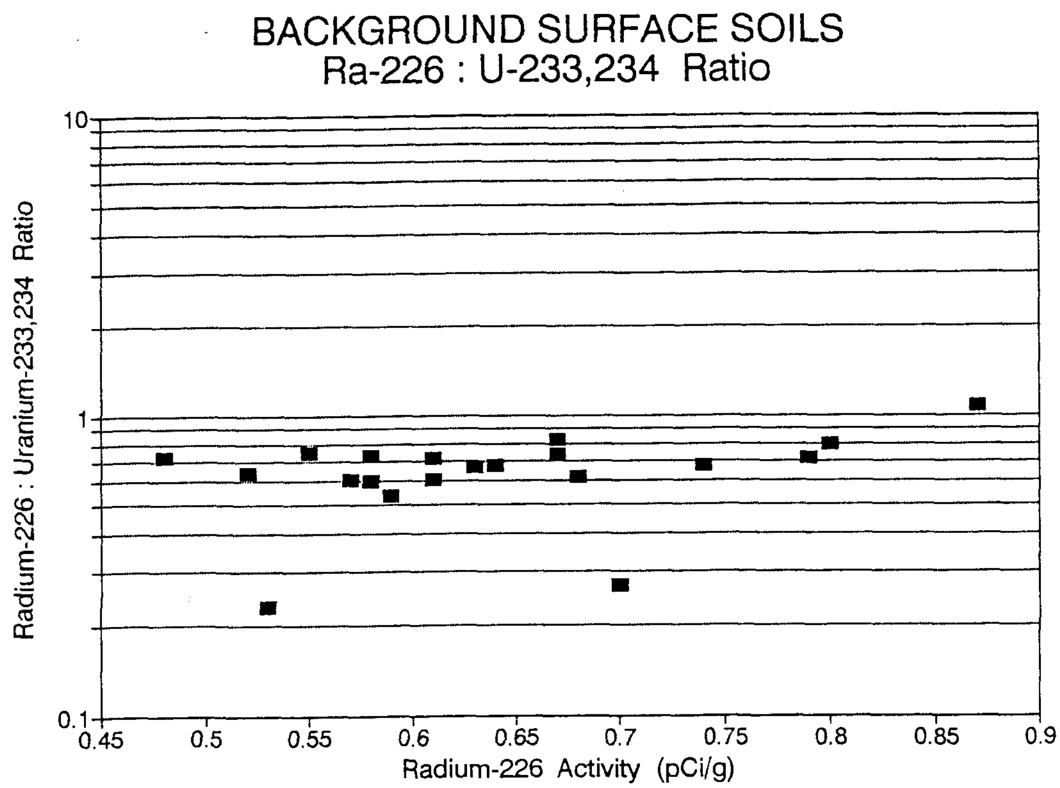
6b


OU4 SUBSURFACE (BOREHOLE) SOILS
Ra-226 : U-233,234 Ratio
Radium-226 : Uranium-233,234 Ratio
10
1
0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Radium-226 Activity (pCi/g)

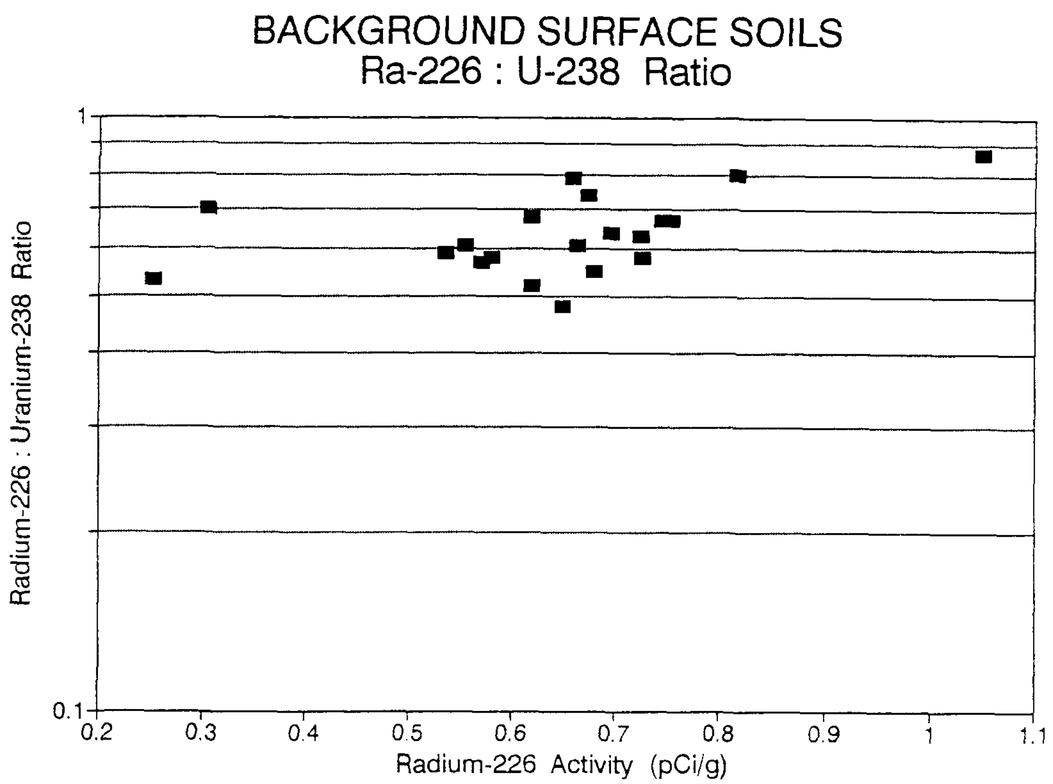
7a


OU4 SUBSURFACE (BOREHOLE) SOILS
Ra-226 : U-238 Ratio
Radium-226 : Uranium-238 Ratio
10
1
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Radium-226 Activity (pCi/g)

7b


BACKGROUND SURFACE SOILS
Ra-226 : U-233,234 Ratio
Radium-226 : Uranium-233,234 Ratio
10
1
0.1
0.45
0.5
0.55
0.6
0.65
0.7
0.75
0.8
0.85
0.9
Radium-226 Activity (pCi/g)

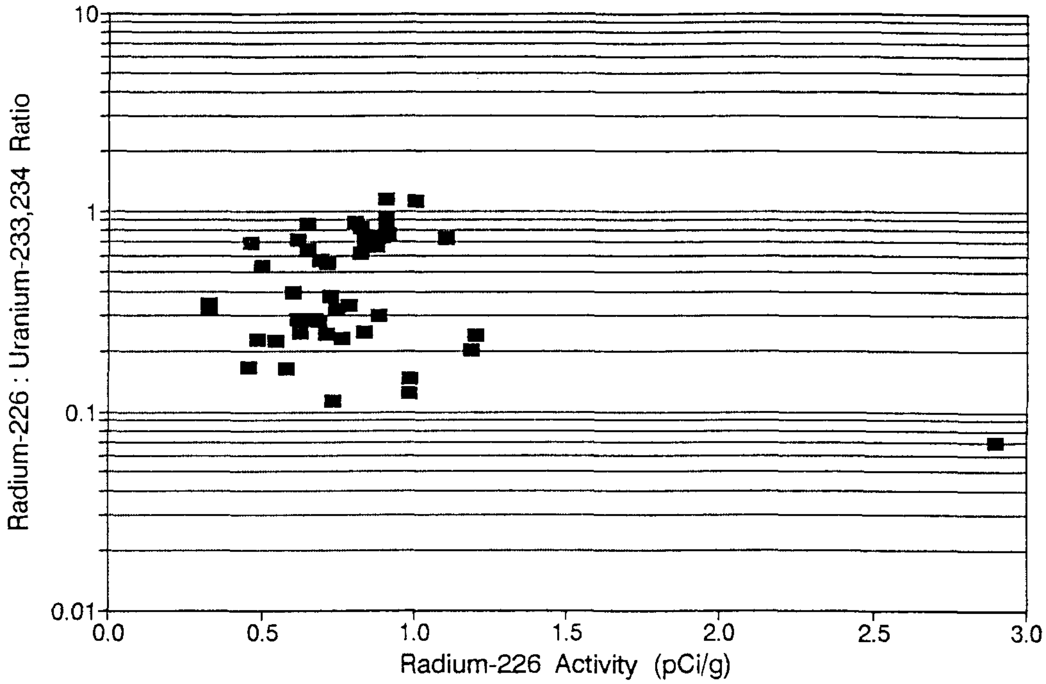
8a


BACKGROUND SURFACE SOILS
Ra-226 : U-238 Ratio
Radium-226 : Uranium-238 Ratio
1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
Radium-226 Activity (pCi/g)

8b

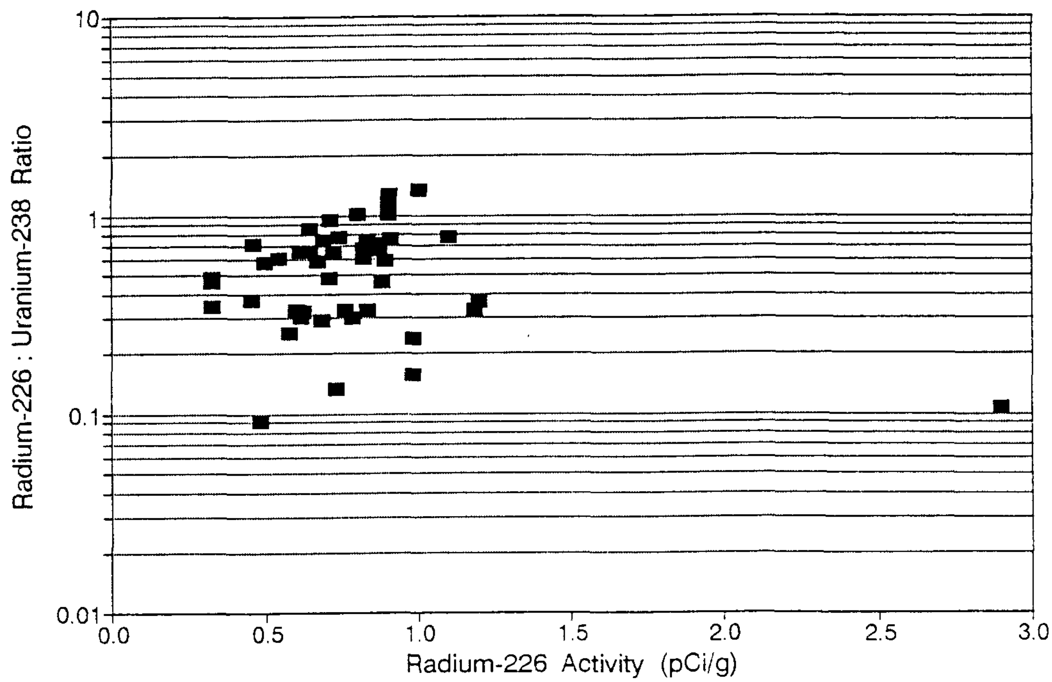
13

OU4 SURFACE SOILS
Ra-226 : U-233,234 Ratio



9a

OU4 SURFACE SOILS
Ra-226 : U-238 Ratio



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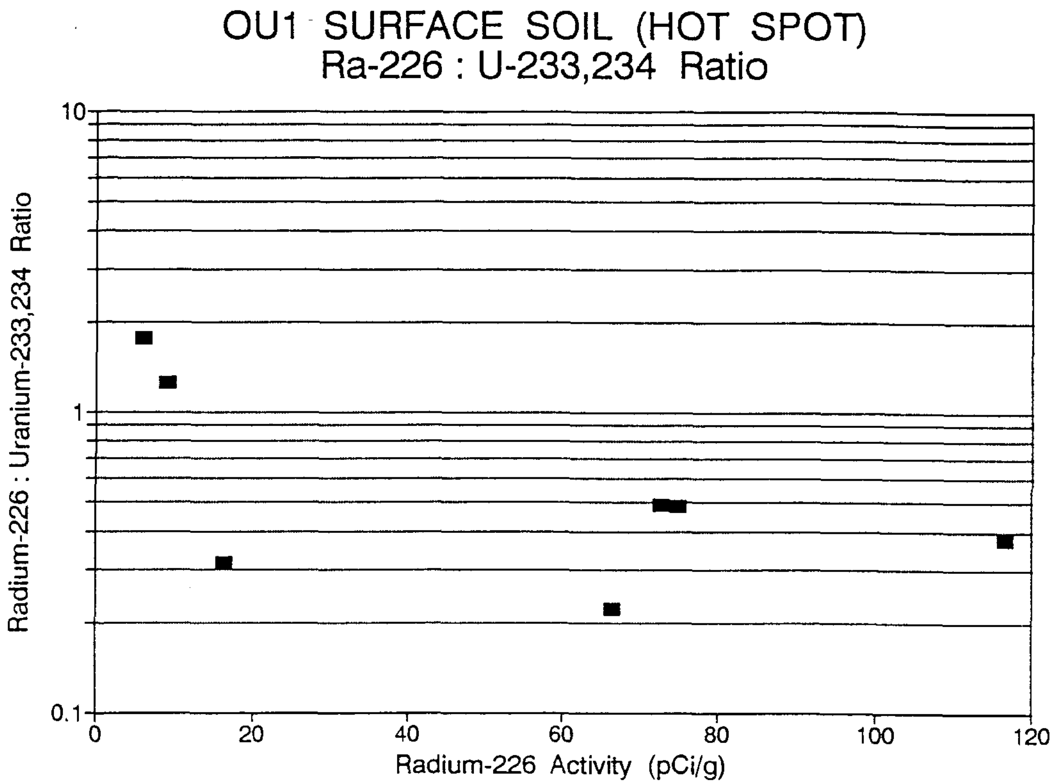
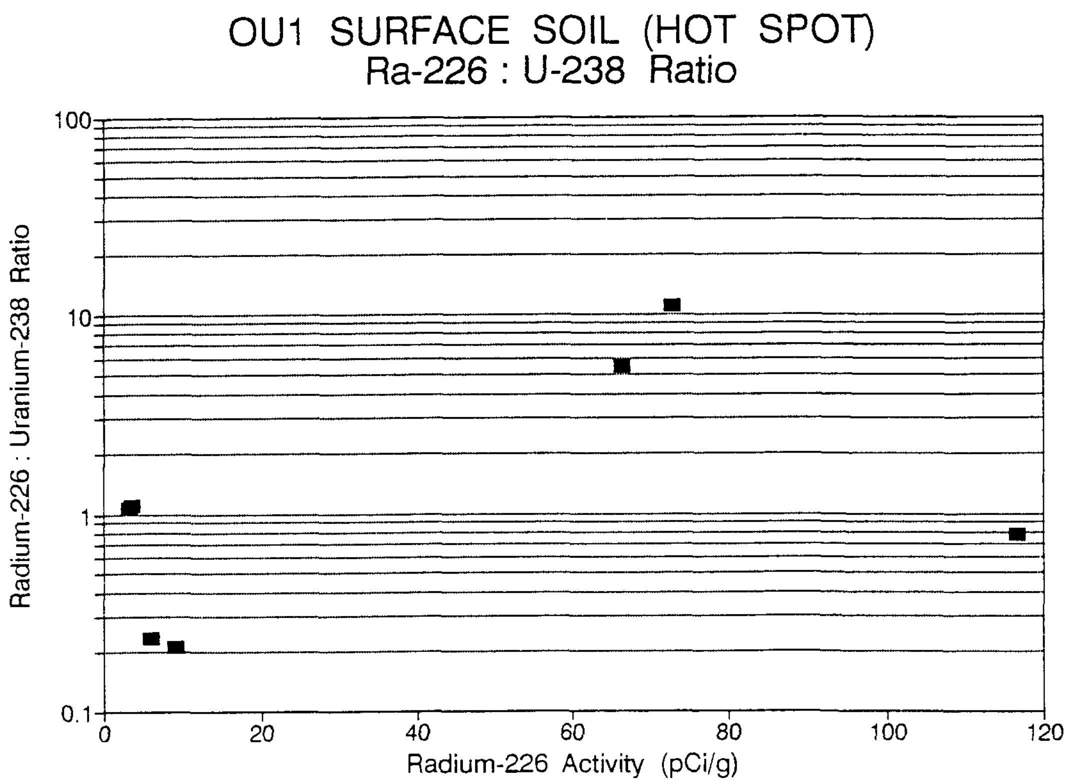

OU1 SURFACE SOIL (HOT SPOT)
Ra-226 : U-233,234 Ratio
Radium-226 : Uranium-233,234 Ratio
10
1
0.1
0
20
40
60
80
100
120
Radium-226 Activity (pCi/g)

10a


OU1 SURFACE SOIL (HOT SPOT)
Ra-226 : U-238 Ratio
Radium-226 : Uranium-238 Ratio
100
10
1
0.1
0
20
40
60
80
100
120
Radium-226 Activity (pCi/g)

10b

15/15